

THE APPLICATION OF INORGANIC MEMBRANES IN HYDROCARBON FUEL CELLS

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1.0 INTRODUCTION

The expansion of laboratory efforts in fuel cells in the last several years has been noted for its urgency and aggressiveness. Three broad categories of fuel cell systems have evolved - the ion membrane, the liquid electrolyte (including electrolytes absorbed in asbestos) and high temperature electrolytes including fused salt matrices and ceramic bodies.

In this paper we shall concentrate on the activities of our laboratories in the area of inorganic ion exchange membranes. For those readers desiring to establish a background in the various organic membrane fuel cell types suitable references are available (1, 2, 3, 4, 5).

It is interesting to note that the first synthetic ion exchangers were also inorganic, i. e., the synthetic zeolites or Permutits⁽⁶⁾. The subsequent development of the organic exchanger resins, with emphasis on practical applications, completely dominated the field of ion exchange chemistry, and it was not until recently that, for the reasons mentioned below, there has been a resurgence of interest in inorganic exchangers and membranes.

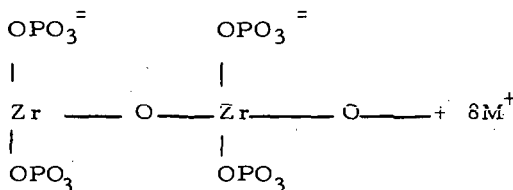
During recent years there has been considerable research on inorganic cation exchangers. The heteropolyacid salts, such as ammonium phosphomolybdate, and the acid salts of hydrous oxides, such as zirconium phosphate have proven to be particularly interesting and their investigation by numerous researchers has been well documented in a monograph by Amphlett⁽⁶⁾. Much less attention has been given to inorganic anion exchangers. Kraus, et al,⁽⁷⁾ as well as Amphlett, ⁽⁸⁾ have investigated the anion exchange properties of various hydrous oxides, particularly the quadrivalent metal oxides, such as ZrO_2 , SnO_2 , ThO_2 , and TiO_2 . Duwell and Shepard⁽⁹⁾ have prepared mixed hydrous oxides anion exchangers in which a second cation of higher valence than the parent cation is introduced into the structure, the resulting net positive charge being balanced by the presence of exchangeable anions. Schoenfeld⁽¹⁰⁾ has done similar research on mixed oxide anion exchangers and has studied the relation between capacity and drying temperature of the precipitated gel.

Preliminary efforts in developing and characterizing inorganic membranes were made by Dravnieks et al⁽¹¹⁾, and Hamlen⁽¹²⁾. Membranes produced during these investigations were essentially non adherent compacts or membranes produced by using teflon as a sintering adhesive. These experimental materials were suitable for obtaining some analytical values but lacked the strength to serve as practical fuel cell membranes. Moreover, they possessed no capability for extended operation at higher temperatures such as $90^\circ - 150^\circ C$. The latter capability is particularly of interest since the temperature range mentioned apparently is at least a minimal practical requirement for hydrocarbon utilization in phosphate based fuel cells⁽¹³⁾. Another implied requirement and one that indeed is most important is the

ability to retain water in the membrane so that efficient electrolyte conductance can be established. It is toward these ends and the attainment of high strength, and high electrolytic conductance and good water retention that the Astropower Laboratories has striven^(14,15). A good measure of success has been achieved and the results are reported below.

The principal membrane activity has been focused on the inorganic polymer, ZrPO_4 . Essentially, the reason for our interest in this polymer is that a good deal of laboratory information exists relative to this material and considerable success has been achieved in these laboratories in developing strong conductive zirconium phosphate. The phosphate group as noted above appears to have interesting properties in hydrocarbon oxidation⁽¹³⁾.

Tests of the cation exchange capacity of zirconium phosphate in these laboratories have duplicated results of other investigators^(7,8). The structure of zirconium phosphate as an inorganic polymer with exchangeable H^+ ions attached to fixed ionic groups has been proposed by other investigators as⁽¹⁶⁾,



where the M^+ are hydrogen ions or exchangeable cations attracted to the negatively charged phosphate groups. It seems reasonable to assume that there are two exchange sites per phosphate group, corresponding to the two dissociable hydrogens, and this assumption was the basis for calculating the theoretical cation exchange capacity of 13.3 meq/g. Table I indicates the theoretical and actual capacities of three cation exchangers⁽¹⁷⁾. The observed capacity of 3.2 meq/g at pH 6, however, would seem to indicate that only one hydrogen per phosphate group is replaceable, and hence the maximum attainable capacity may be 6.65 meq/g. Kräus⁽⁷⁾ has made similar observations concerning the number of replaceable hydrogens.

Clearly a number of acid salts may have utility as hydrogen-oxygen fuel cells as well as having applications in hydrocarbon fuel cells. The investigation of such salts has been performed in these laboratories⁽¹⁵⁾ and by European investigators⁽¹⁸⁾. The latter made successful fuel cell membranes from tin and titanium phosphates by joining the particulate phosphates with organic binders such as carboxymethyl cellulose. The membranes gave satisfactory results at 25°C but do not appear satisfactory for applications at elevated temperatures.

The use of solid acid phosphate membranes has advantages over liquid phosphoric acid as an electrolyte medium for hydrocarbon oxidation. Principally, these are compactness, position insensitivity, and, in particular, lack of corrosive attack. In the investigation of these membranes several technical factors have combined to furnish us with a good solid electrolyte for hydrocarbon utilization and testing. These are:

1. Special techniques for forming strong cohesive membranes⁽¹⁵⁾.
2. The attainment of high conductivities⁽¹⁴⁾.

3. The ability, if required to implant catalyst materials directly in the membrane^(14, 15).
4. The incorporation of water balancing agents, which enable the fuel cell electrolyte to operate as high as 150°C⁽¹⁵⁾.
5. Hydrolysis tests indicating the inherent stability of the inorganic phosphate membrane⁽¹⁴⁾.

2.0 EXPERIMENTAL

2.1 Membrane Preparation - Non-Sandwich Type

A 1:1 - mixture ratio of ZrO_2 and H_3PO_4 was prepared and sintered at a temperature of 500°C. The sintered materials were crushed and ground to minus 80 mesh and mixed with equal parts of H_3PO_4 and "Zeolon H" a Norton Company sieve material. The "Zeolon H" is one of a group of water balancing agents developed and used at Astropower Laboratory in these experiments⁽¹⁵⁾. These mixtures were dried for 16 hours at 130°C and then granulated to minus 32 plus 80 mesh. Next, they were pressed at 15-ton load into 2-in. diameter membranes having the thickness of the order of 0.7 mm. Finally they were sintered at temperatures of 500°C for two hours. The transverse break strengths of these resulting membranes were determined and were about 5000 psi \pm 100. The resistivities of the membrane was about 4 ohm-cm at 110°C and 100% R. H.

2.2 Membrane Preparation - Sandwich Type

Basically, this technique involves the formation of a fuel cell membrane catalyst composite consisting of three layers of material which are pressed and sintered together. The center layer is comprised of membrane material similar to the mix described in 2.1, and the two outer layers which are bonded to the center layer are mixtures of the same membrane material and platinum black. The composite three-sectional membrane was formed in the following manner:

A weighed amount of the platinum-bearing material is placed in the pressing die, followed by a layer of the membrane material and a second layer of the catalyst-bearing material. The top punch is then inserted and the assembly (two-inch diameter) is pressed at 15 tons total load. After pressing the composites are placed on flat, smooth refractory plates and sintered in air for two hours at 500°C. After cooling to room temperature, the composite membrane-catalyst wafer was impregnated with 85% phosphoric acid, oven-dried at 120°C and sintered at 500°C for two hours. This impregnation procedure was repeated two more times.

2.3 Fuel Cell Assembly and Operation

A design of a typical fuel cell unit is shown in Figure 1. Assembly of the fuel cell is performed by placing either type of membrane in the recessed metal casing which has been treated with a film of silicone resin. Platinum or palladium powder is sprinkled on both surfaces of the membrane and screen electrodes pressed up against the catalyst on either side. When sandwich membranes are used, additional catalyst is not required. The catalyst loading is a total of .025 g. cm⁻². The O-rings are put in place and the assembly bolted together. The flow rate of the hydrocarbon is 2 cm³ min.⁻¹ and for oxygen 4 cm³ min.⁻¹. The entire configuration is operated in an oven in the temperature range 50° - 150°C.

3.0 RESULTS

The performance of the fuel cell configuration when fueled with hydrogen and oxygen were encouraging in proving the capability for operation of the "water" balanced zirconium phosphate in the temperature range extending from about 50°C to 150°C. Some of the results obtained for the hydrogen-oxygen system are shown in Figure 2. The duration of the fuel cell performance depicted graphically range from 300 - 1000 hours⁽¹⁴⁾. The stable performance of the system over the 50°C - 150°C led us to believe that it was suitable for preliminary tests as a hydrocarbon fuel cell.⁽¹⁵⁾

Efforts were then initiated with hydrocarbon fuels and oxygen. These were ethane, propane, butane and propylene. Pertinent data is shown in Figure 3 for propylene, Figure 4 for ethane, Figure 5 for propane and Figure 6 for butane. Polarization points were recorded after five minutes of stabilized performance.

4.0 DISCUSSION

Figure 2 is illustrative of the fact that the membrane system employed is functional over the range 50° - 150°C. Attempts to move to higher temperatures have led to deterioration of fuel cell performance. This can be attributed to the lack of effectiveness of the "water balancing" agent contained in the membrane. A secondary effect, perhaps, is that the partial pressure of water in the vicinity of the electrode-catalyst may thereby become considerably higher, making access of the hydrocarbon and oxygen to the reaction interface more difficult.

Figure 3 for propylene indicates that performance of the hydrocarbon fuel cell appears to improve with elevated temperature, (as would be anticipated) until the vicinity of 150°C is attained. This does not preclude improved performance (with temperature) but indicates that a satisfactory electrolytic conductive mechanism could not be maintained at 150°C due to "water balancing" agent deficiency. Tests in these laboratories⁽¹⁵⁾ have indicated that other "water balancing" materials may be more effective.

5.0 CONCLUSIONS

1. The essential element in the maintenance of an electrolytic conductance in a fuel cell membrane at elevated temperatures is the presence of a water balancing agent. An exception may be that the membrane itself may have this property.
2. Phosphate based inorganic membranes serve as a suitable electrolytic environment for hydrocarbon oxidation in fuel cells between 100 - 150°C.

6.0 ACKNOWLEDGMENTS

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TABLE I
THEORETICAL AND OBSERVED CAPACITIES
FOR INORGANIC CATION EXCHANGERS

<u>Gel</u>	<u>Assumed Mathematical Ratios for Calculating Theoret. Capacity</u>	<u>Molecular Weight</u>	<u>Theoret. Capacity</u>	<u>Observed Capacity (meq/g)</u>
Zirconium phosphate	$\begin{array}{c} \text{H}^+ \\ \\ \text{H}^+ \text{OPO}_3 = \\ \\ -\text{Zr}-\text{O}- \\ \\ \text{H}^+ \text{OPO}_3 = \\ \\ \text{H}^+ \end{array} \quad n$	301n	13.3 (6.65)*	3.2
Zirconium tungstate	$\begin{array}{c} \text{H}^+ \\ \\ \text{H}^+ \text{QWO}_3^- \\ \\ -\text{Zr}-\text{O}- \\ \\ \text{H}^+ \text{OWO}_3^- \end{array} \quad n$	605n	3.3	2.1
Thorium phosphate	$\begin{array}{c} \text{H}^+ \\ \\ \text{H}^+ \text{OPO}_3 = \\ \\ -\text{Th}-\text{O}- \\ \\ \text{H}^+ \text{OPO}_3 = \\ \\ \text{H}^+ \end{array} \quad n$	442n	9.05 (4.52)*	2.0

*Value in parentheses represents theoretical capacity if only one hydrogen ion per phosphate group is exchangeable.

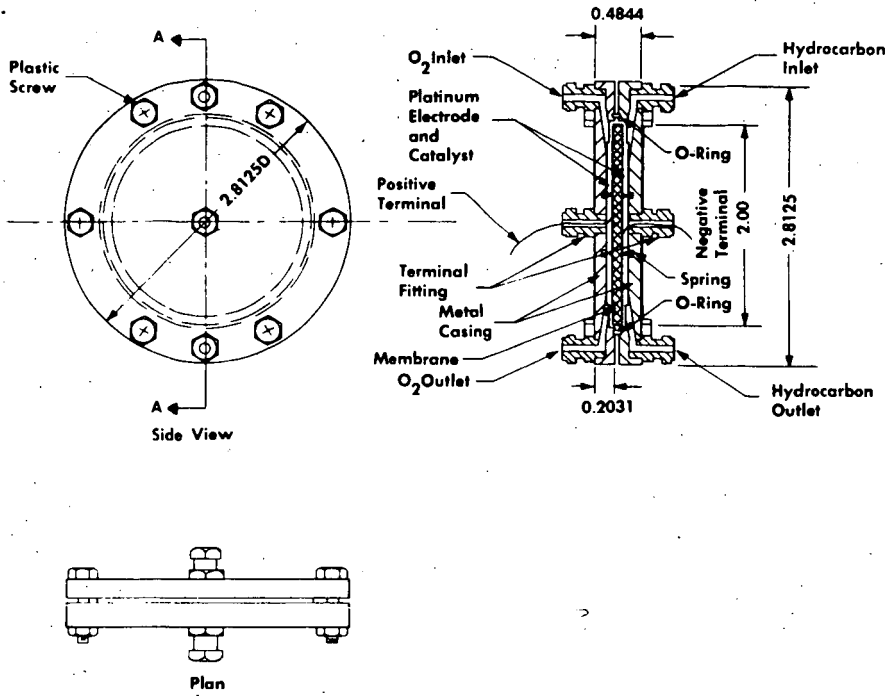


Figure 1. Hydrocarbon Test Fuel Cell

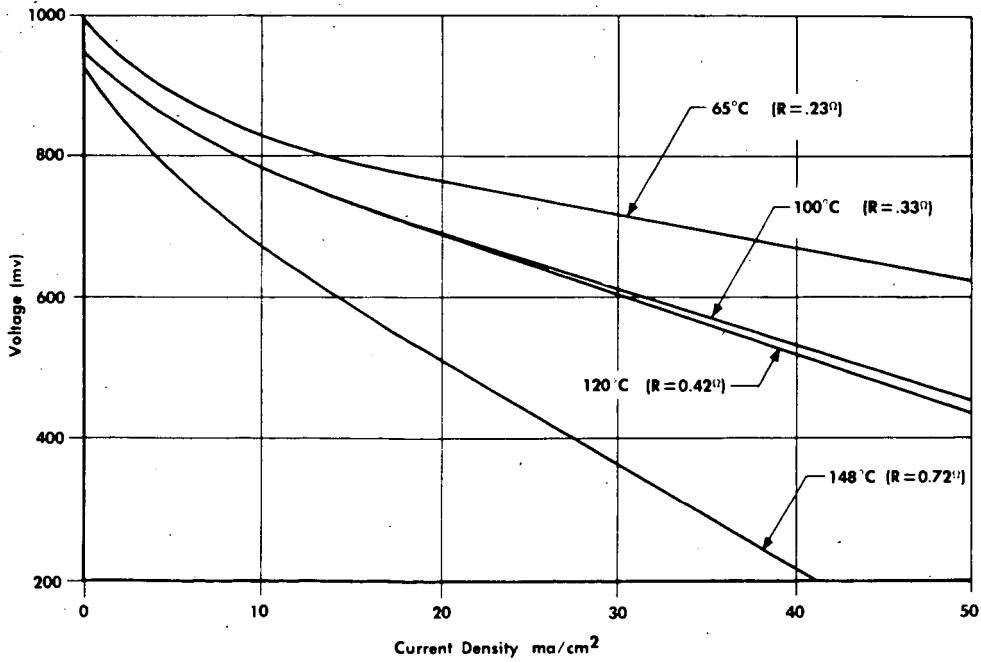


Figure 2. Polarization Curves for Hydrogen-Oxygen Inorganic Membrane Fuel Cell

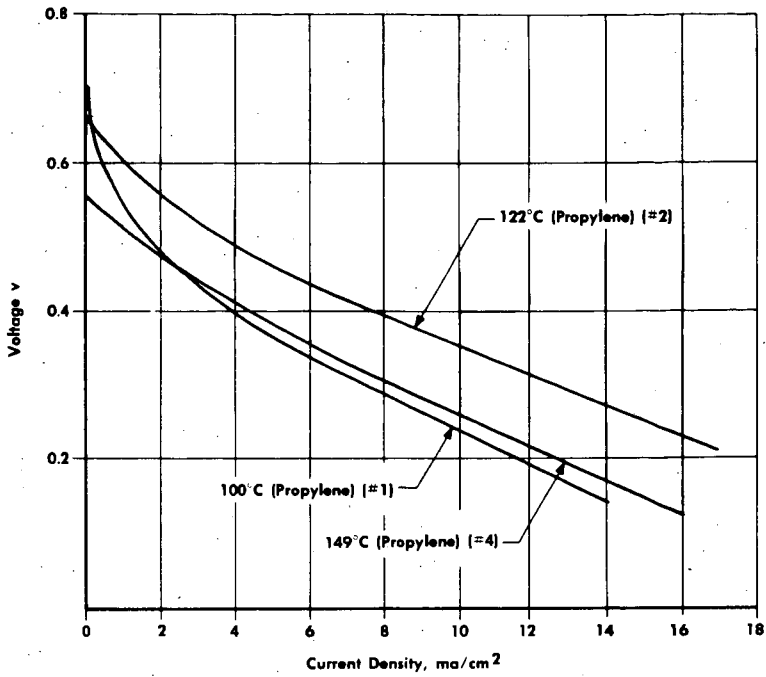


Figure 3. Polarization Curves for Propylene-Oxygen Inorganic Membrane Fuel Cell

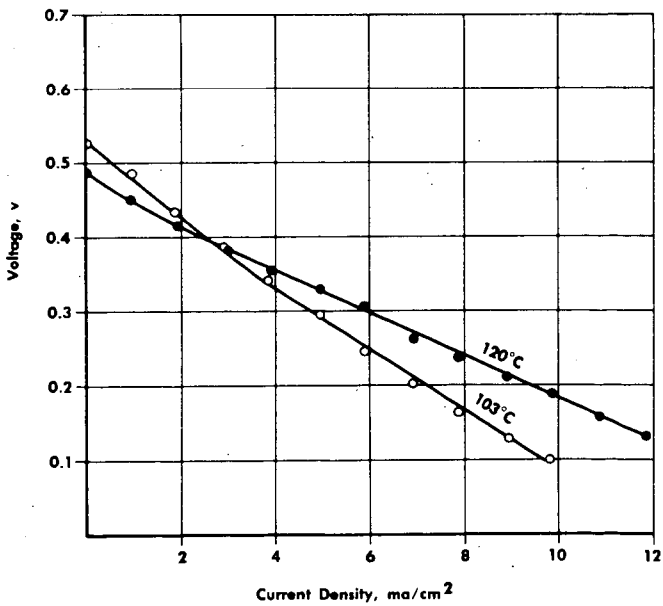


Figure 4. Polarization Curve for Ethane-Oxygen Inorganic Membrane Fuel Cell

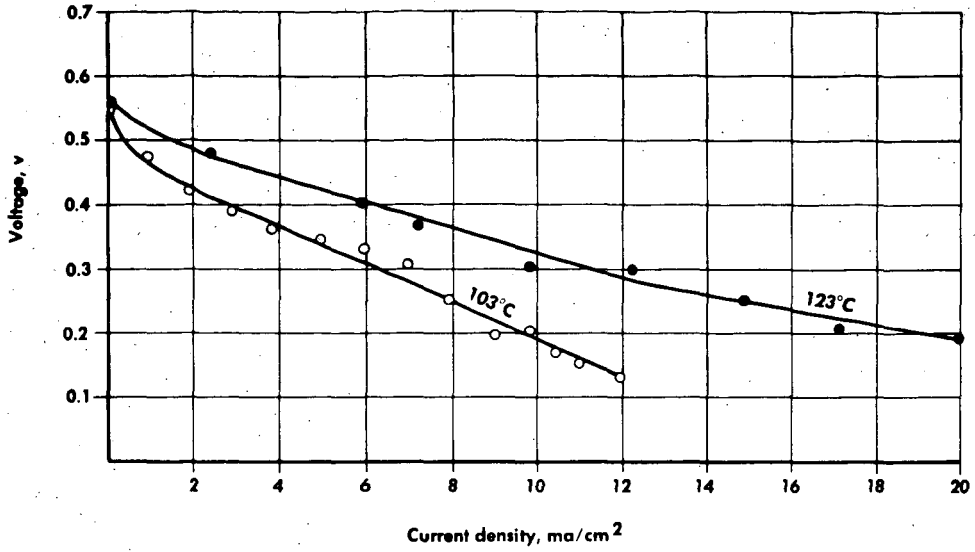


Figure 5. Polarization Curves for Propane-Oxygen Inorganic Membrane Fuel Cell

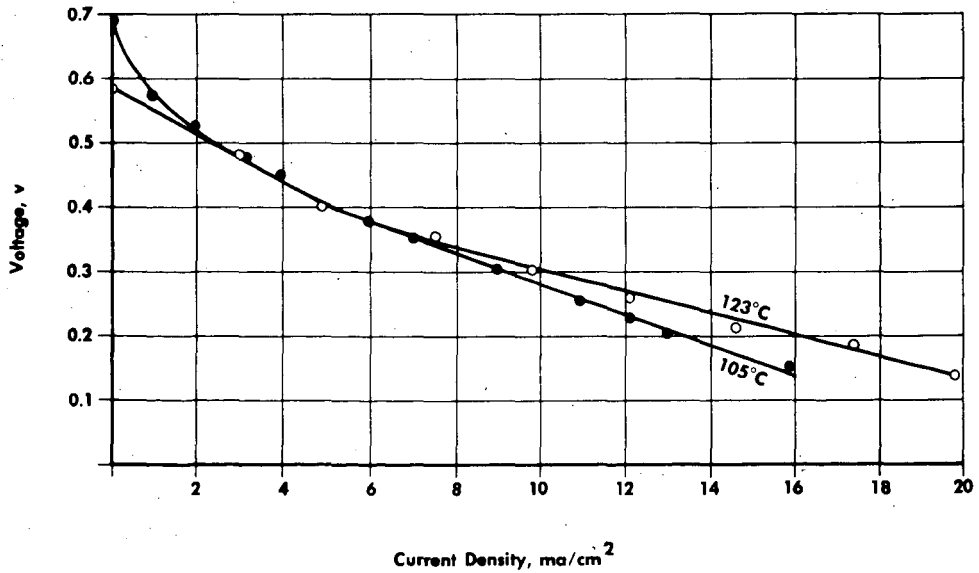


Figure 6. Polarization Curves for Inorganic Membrane Butane-Oxygen Fuel Cell